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Low-pressure Environmental TEM (ETEM) studies of Au assisted MgO nanorod growth

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Over the past few decades, there has been an increasing interest in the use of supported nanoparticles in applications ranging from drug delivery to catalysis. The functionality of such nanoparticles is to a large extent controlled by their shape and exposed surface facets. However, information about the crystal structure of their surfaces is often obtained from measurements that are averaged over large numbers of particles. Furthermore, the catalytic activity depends on the support and hence on the interaction between support and catalyst nanoparticle.

Supported Au nanoparticles are active catalysts for the low temperature oxidation of carbon monoxide [1]. Density functional theory and Monte Carlo calculations have been used to predict their equilibrium shapes [2] and their CO-adsorption-induced reshaping [3]. Reshaping of the Au particles is predicted to occur precisely in the size regime where they become inactive for CO oxidation.

Here, we present an environmental transmission electron microscopy (ETEM) study of shape changes of Au nanoparticles supported on MgO in a controlled gas atmosphere, in order to elucidate the mobility of surface species and the configuration of the Au/MgO interface. The particles are synthesized by depositing a thin layer of Au onto MgO smoke particles. The Au agglomerates into particles that are a few nanometers in size, providing a model system for the investigation of nanoparticle surface and interface properties.

Ajayan et al. [4], Kizuka [5] and Nasibulin et al. [6] reported growth of nanorods on MgO smoke particles driven by the electron beam in high vacuum. However, the growth is strongly dependent on the gaseous environment. Here we investigate the relation between the surrounding environment and MgO nanorod growth.

The electron beam induced growth of MgO nanorods is studied over a pressure range from UHV 10^{-9}mbar to 10^{-4}mbar focusing on shape changes and growth rates with respect to changes in pressure, gas atmosphere and beam current density.

Aberration corrected ETEM provides a unique opportunity to study and characterize the surface and interface structure of supported nanoparticles in a controlled environment [7]. This allows for a deeper understanding of the dynamic response of the surface and interface to changes in gas composition, pressure and temperature.

Additionally, an Ultra High Vacuum (UHV) TEM has been used in order to have a higher degree of control of the initial state and probe the low-pressure regime. This combination is a powerful toolbox for charactering the behavior of the mobility of atomic species at the MgO surface leading to the formation of nanorods.

Figure 1 shows Au particles on MgO cubes being irradiated by a 300keV electron beam with a residual pressure of 10^{-6}mbar and a current density 10^{-1}A/cm^2. Over a period of one hour, growth of MgO nanorods catalyzed by Au nanoparticles is observed. Eventually the Au nanoparticles fall off, leaving the MgO nanorods for beam induced dissolution. Figure 2 shows the development of the length of a set of nanorods over a period of 2 hours for a fixed water vapour pressure and a fixed beam current density.

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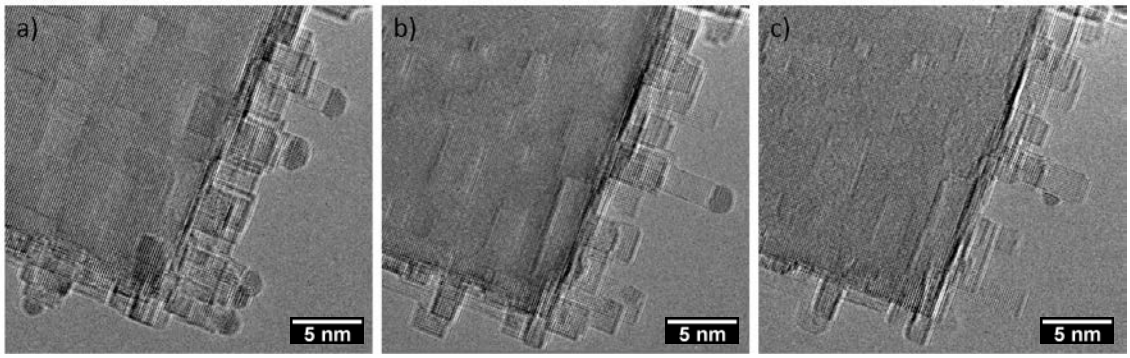

Figure 1: *Au particles on MgO irradiated by 300keV electrons (current density of 10^{-1}A/cm²) with a residual pressure of 10^{-6}mbar. (a) initial state, (b) after ca. 40 min, and (c) after ca. 1 hour.*

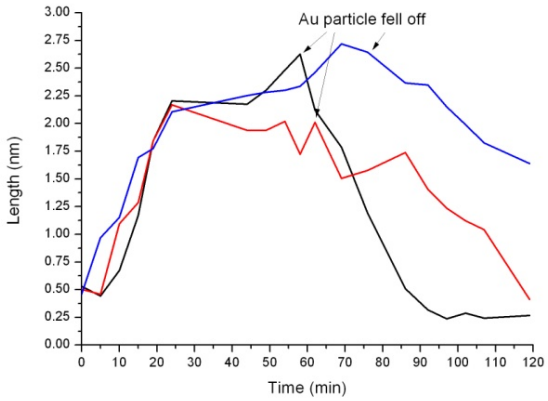

Figure 2: *Length development of a set of MgO nanorods grown at Au particles irradiated by 300keV electrons (current density of 10^{-1}A/cm²) with a residual pressure of 10^{-6}mbar. The beam induced growth is halted and turned into dissolution when the Au particles fell off.*